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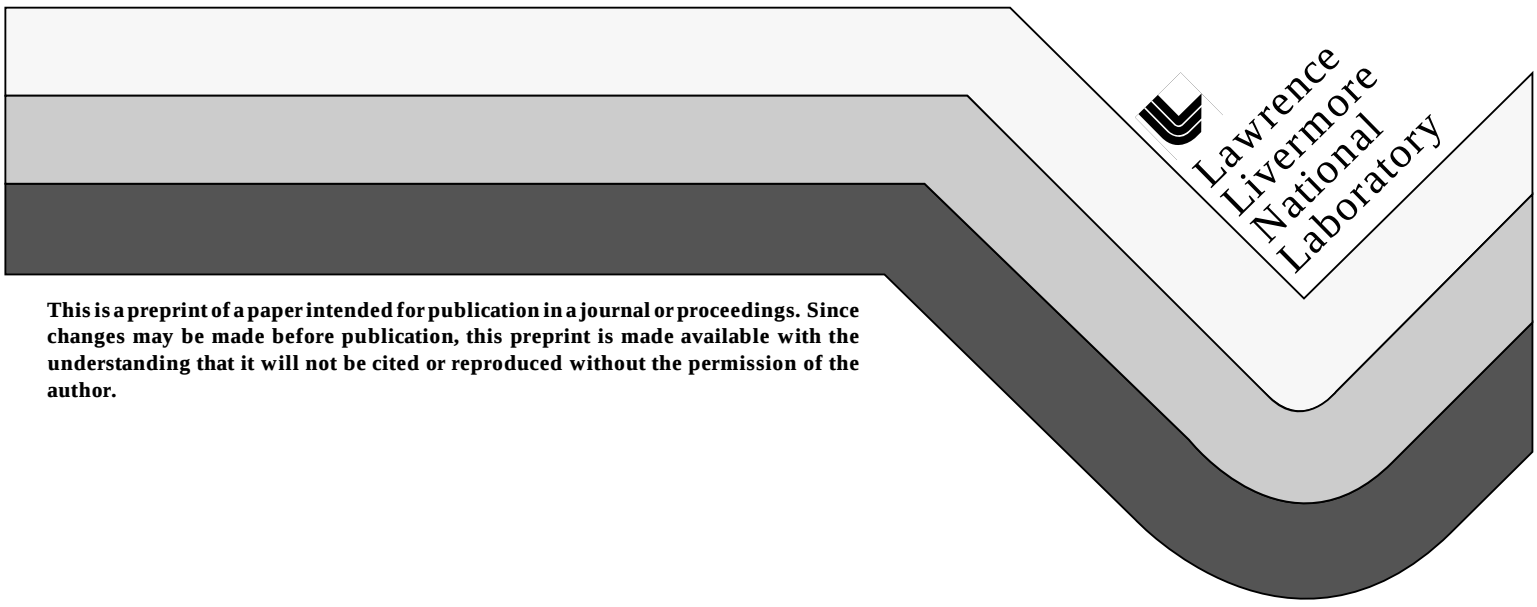

Numerical Study of Ethylene and Acetylene Laminar Flame Speeds

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Abstract

Detailed chemical kinetic computations for ethylene-air and acetylene-air mixtures have been performed to simulate laminar flame speeds. Sensitivity analysis was applied to determine those reactions which strongly influence flame propagation. In ethylene-air mixtures, the $C_2H_3 + O_2 = CH_2CHO + O$ reaction was one of the most sensitive reactions in the C_2H_4 / C_2H_3 submechanism and therefore this reaction was very important to ethylene flame propagation. This reaction was not considered in previously reported mechanisms used to model ethylene-air flame propagation. In acetylene-air mixtures, the $C_2H_2+O\rightarrow$ Products, $HCCO+H=CH_2(s)+CO$, $HCCO+O_2=CO_2+CO+H$, $H+C_2H_2(+M) = C_2H_3(+M)$ and $CH_2(s)+C_2H_2 = H_2CCCH+H$ were the most sensitive reactions in the C_2H_2 / HCCO / $CH_2(s)$ reaction set.

Introduction

Ethylene and acetylene are important intermediates in the combustion of larger aliphatic compounds. Consequently, it is important to validate the chemical kinetic mechanisms of these intermediates in order to treat properly the oxidation of their largest aliphatic parents. The proper prediction of laminar flame speed is one step toward this validation. In this paper, laminar flame speed modeling results for ethylene-air and acetylene-air mixtures are presented and compared to experimentally published values. The reactions that control flame speed for ethylene and acetylene are identified.

Results

A detailed C_3 hydrocarbon mechanism consisting of 46 species and 246 reversible reactions is used in a one-dimensional, pre-mixed, laminar flame code (PREMIX) with transport [1,2]. The chemical kinetic mechanism is based on the previous work by the authors [3,4] and has been modified as discussed below. In figure 1, numerical calculations show very good agreement with the experimental laminar flame speed data [5-7] for a wide range of ethylene-air and acetylene-air stoichiometries. A flame speed maximum of 70.0 cm/sec at an ethylene-air equivalence ratio of 1.1 and atmospheric pressure was calculated, and is in agreement with the measured data. The ethylene-air sensitivity analysis results are shown in figure 2 for equivalence ratios of 0.6, 1.0 and 1.4. If the reaction rate constant is increased, positive sensitivity coefficients indicate the mass burn rate (flame speed) will increase and negative coefficients indicate the mass burn rate (flame speed) will decrease. Mass burn rate sensitivity analysis determined the $H + O_2 = OH + O$, $HCO + M = H + CO + M$, $CO + OH = CO_2 + H$, $C_2H_3 + O_2 = CH_2CHO + H$, $C_2H_4 + H = C_2H_3 + H_2$ and $C_2H_4 + OH = C_2H_3 + H_2O$ reactions were the most sensitive toward promoting flame propagation in ethylene-air

mixtures as denoted by their positive sensitivity coefficient. Chain terminating reactions or reactions producing HO_2 retarded flame propagation as denoted by the negative sensitivity coefficient.

For the acetylene-air study, a flame speed maximum of 152.4 cm/sec at a fuel-air equivalence ratio of 1.3 and atmospheric pressure was calculated and is in agreement with the measured data as shown in figure 3. The sensitivity analysis results for acetylene-air mixtures are shown in figure 4. Mass burn rate sensitivity analysis of acetylene-air laminar flame speeds determined the $H + O_2 = OH + O$ chain branching reaction and reactions producing H-atoms, $CO + OH = CO_2 + H$, $C_2H_2 + O = HCCO + H$, $HCCO + O_2 = CO_2 + CO + H$, $HCO + M = H + CO + M$, and $C_2H_2 + CH_2(s) = H_2CCCH + H$ promoted flame propagation. The $HCCO + H = CH_2(s) + CO$, $H + C_2H_2 (+M) = C_2H_3 (+M)$ and $HCO + H = CO + H_2$ reactions removed H-atoms from the free radical pool, thereby, retarding flame propagation. The results showed sensitivity to the branching ratio of $C_2H_2 + O = CH_2 + CO$ and $C_2H_2 + O =$ HCCO + H. The products HCCO + H enhance flame propagation through H-atom production.

The kinetic rates used for the most sensitive reactions in the C_3 hydrocarbon mechanism are listed in Table 1. The forward rate is reported along with its source, and the reverse rate is calculated through equilibrium rate constants. Thermochemistry was obtained from the Chemkin Thermochemical Database [8] with heat of formation and entropy modifications made to the C_2H_5, C_2H_3, $CH_2(s)$ and CH_2 species. The revised heat of formation and entropy values are $\Delta H_f(C_2H_5,298K) =$ 28.73 kcal/mol [9], $\Delta H_f(C_2H_3,298K) = 70.4$ kcal/mol [10], $\Delta H_f(CH_2(s),298K) = 101.9$ kcal/mol, $\Delta H_f(CH_2,298K) = 92.9$ kcal/mol [11] and $S(C_2H_5, 298K) = 59.03$ kcal/mol-K [9]. The following discussion reports on the important considerations / results involving the kinetic rate choices for ethylene - air and acetylene - air flame speed modeling.

$H+O_2 = OH+O$ Reaction: This reaction is most important in flame propagation phenomena for all hydrocarbon - air mixtures. The recent measurements of Du and Hessler [12] have confirmed the earlier kinetic rate determination of Masten et al. [13] in both the forward and reverse directions. This study used the Masten et al. kinetic rate in the exothermic direction.

$CO+OH = CO_2+H$ Reaction: This reaction is most sensitive in fuel-lean ethylene - air and acetylene - air mixtures. The prompt CO production in both fuels allowed CO oxidation by hydroxyl to promote flame propagation due to its H-atom production capability. This study used the recommended kinetic rate of Zellner [14] which is in good agreement with the recent measurements of Wooldridge et al. [15] for this reaction. The Baulch et al. [16] recommended kinetic rate for this reaction predicted flame speeds approximately ~7.0 cm/sec too fast in $\phi = 0.6$ acetylene-air and ethylene-air mixtures.

$C_2H_3+O_2$ = Products Reaction: In our earlier study [3], we showed the $C_2H_3 + O_2 = CH_2CHO + O$ reaction to be important and the $C_2H_3 + O_2 = C_2H_2 + HO_2$ reaction to be unimportant for ethylene oxidation under jet-stirred reactor conditions. We have simultaneously modeled the ethylene - air laminar flame speeds and our earlier jet-stirred reactor work. The $C_2H_3 + O_2 = CH_2CHO + O$ reaction exhibits high sensitivity within the C_2H_4 / C_2H_3 submechanism and is needed for good agreement with the experimental laminar flame speed data.

C_2H_2+O = Products Reaction: The branching ratio for this reaction has been reported to vary from $k_{C2H2+O=HCCO+H}$ / k_{TOTAL} = 0.1 to 0.97 [17]. Recent studies by Peeters et al. [18] at 290K and, Michael and Wagner [19] at 900K -1200K have determined branching ratios of 0.83 and 0.80 respectively. The branching ratio for this reaction is extremely important as CH_2(s) (made from reaction 16 in Table 1) may be considered a prime precursor of aromatics in rich hydrocarbon flames [20]. The branching ratio values of 0.2 and 0.5 underpredicted the experimental acetylene - air flame speed data by ~20 cm/sec and ~10 cm/sec respectively at ϕ = 1.0. Best agreement was attained with a branching ratio of 0.80.

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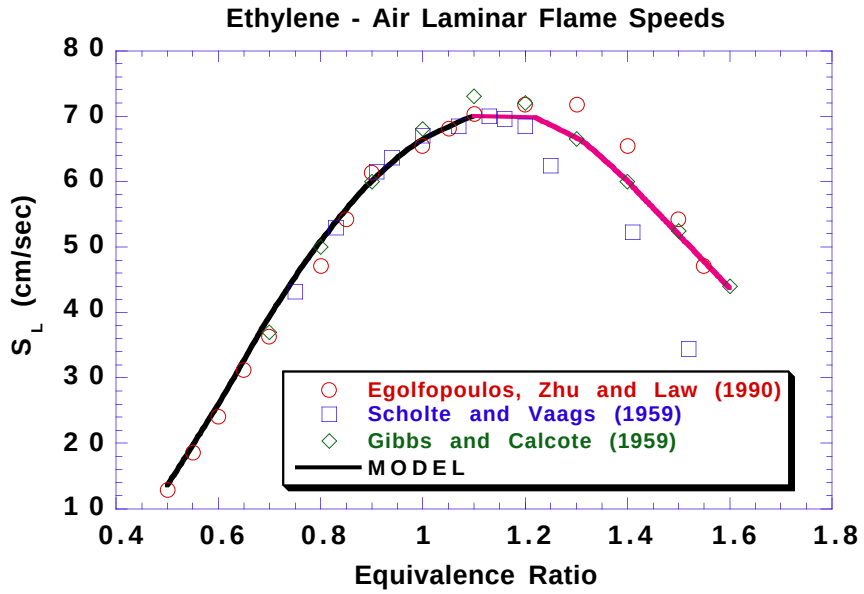

Figure 1. Ethylene - air laminar flame speeds at 1 atmosphere and T_U = 298K as a function of equivalence ratio. Equivalence ratio range 0.5 to 1.6. Comparison between experimental data [5-7] (symbols) and computations (solid line).

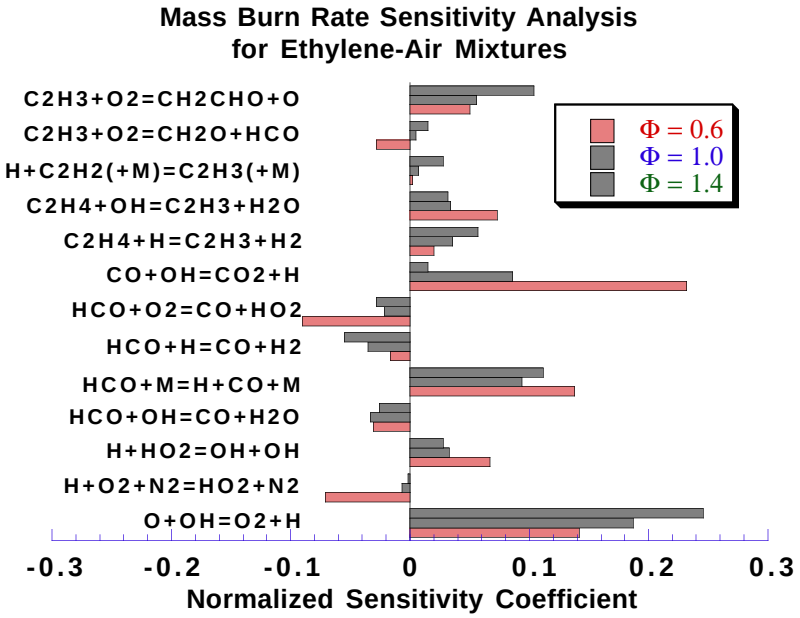

Figure 2. Sensitivity analysis of ethylene - air mass burn rates at 1 atmosphere and T_U = 298K. Normalized first order sensitivity coefficients given by (A_i / m_L) $(\Delta m_L / \Delta A_i)$ where A_i is the pre- exponential factor to the rate constant of the i-th reaction and m_L is the mass burn rate ($m_L = \rho_U S_L$).

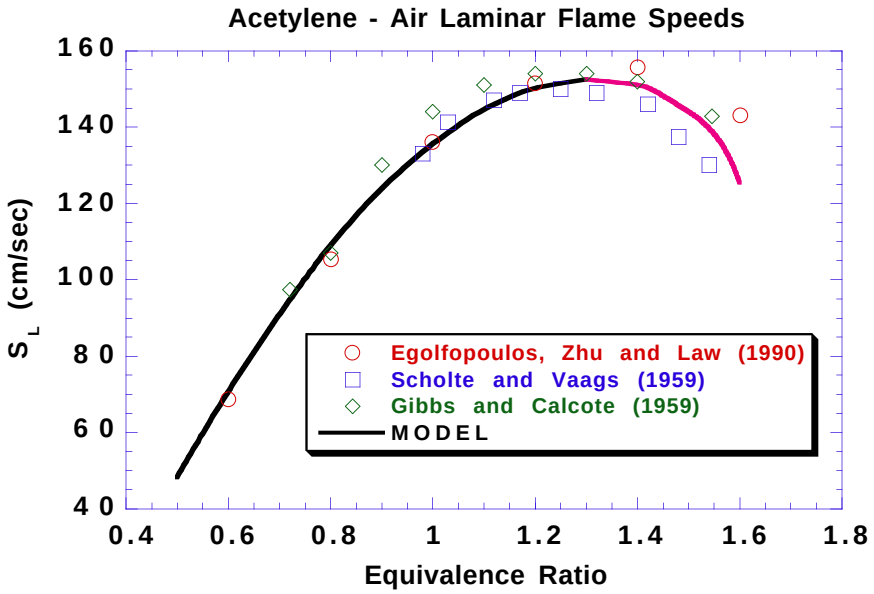

Figure 3. Acetylene - air laminar flame speeds at 1 atmosphere and T_u = 298K as a function of equivalence ratio. Equivalence ratio range 0.5 to 1.6. Comparison between experimental data [5-7] (symbols) and computations (solid line).

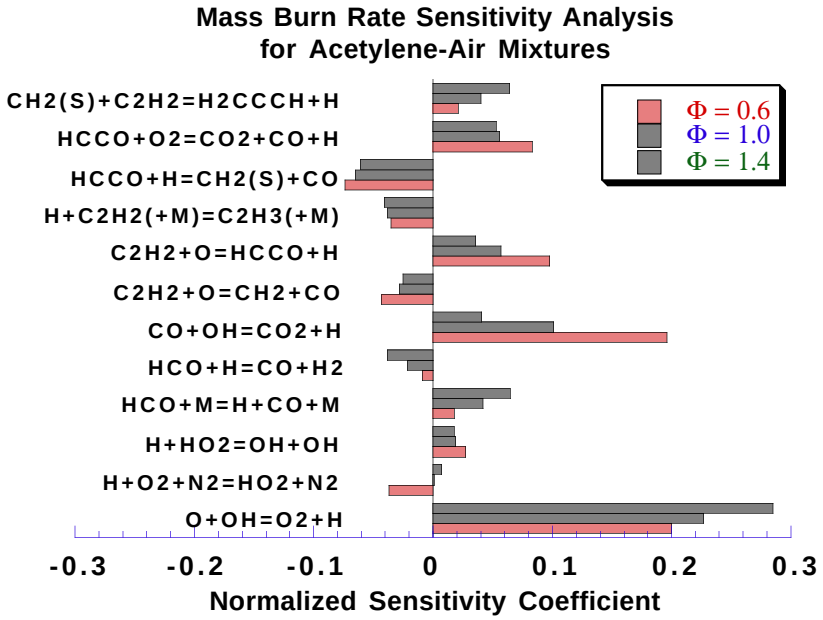

Figure 4. Sensitivity analysis of acetylene - air mass burn rates at 1 atmosphere and T_u = 298K. Normalized first order sensitivity coefficients given by $(A_i / m_L) (\Delta m_L / \Delta A_i)$ where A_i is the pre-exponential factor to the rate constant of the i-th reaction and m_L is the mass burn rate ($m_L = \rho_u S_L$).

Table 1
Rate Constants used for the Most Sensitive Reactions in the C_3 Hydrocarbon Mechanism

Units are cm^3 - mole - sec - kcal - K

$k = A\ T^n \exp(-E_a/RT)$

No.	Reaction	A_{fwd}	n_{fwd}	$E_{a,fwd}$	Reference
1.	$O + OH = O_2 + H$	2.02E+14	-0.40	0.0	JPC,**94**,7119,1990
2.	$H + O_2 + N_2 = HO_2 + N_2$	k_0 = 2.031E+20 $T^{-1.590}$			Compiled Fit [4]
		k_∞ = 4.517E+13			JPC,**89**,342,1985
3.	$H + HO_2 = OH + OH$	1.50E+14	0.00	1.000	[4]
4.	$HCO + OH = CO + H_2O$	1.00E+14	0.00	0.000	JPCRD,**21**,411,1992
5.	$HCO + M = H + CO + M$(a,b)	1.86E+17	-1.0	17.0	JPC,**91**,5325,1987
6.	$HCO + H = CO + H_2$	1.19E+13	0.25	0.0	21st SICP,721, 1988
7.	$HCO + O_2 = CO + HO_2$	7.58E+12	0.0	0.410	JPC, **92**, 651, 1988
8.	$CO + OH = CO2 + H$	9.42E+3	2.25	-2.351	JPC, **83**, 18, 1979 (c)
9.	$C_2H_4 + H = C_2H_3 + H_2$	3.36E- 7	6.0	1.692	IJCK,**23**,437, 1991
10.	$C_2H_4 + OH = C_2H_3 + H_2O$	2.02E+13	0.0	5.936	CPL, **143**, 510, 1988
11.	$H + C_2H_2 (+M) = C_2H_3 (+M)$(d)	k_0 = 1.585E+39 $T^{-7.269}$exp(-6.577/RT) (e,f)			
		k_∞ = 1.567E+13 exp(-2.719/RT)			
		Troe Parameters / a=1.0 T***=1.E-15 T*=2500. T**=1.E+15 /			
12.	$C_2H_3 + O_2 = CH_2O + HCO$	1.09E+23	-3.29	3.892	JPC,**97**,4427,1993
13.	$C_2H_3 + O_2 = CH_2CHO + O$	1.32E+15	-0.78	3.135	(g)
14.	$C_2H_2 + O = CH_2 + CO$	6.116E+6	2.00	1.900	CF,**91**,21,1992 (h)
15.	$C_2H_2 + O = HCCO + H$	1.427E+7	2.00	1.900	CF,**91**,21,1992 (h)
16.	$HCCO + H = CH_2(S) + CO$	1.00E+14	0.00	0.00	CF,**91**,21,1992
17.	$HCCO + O_2 = CO_2 + CO + H$	1.40E+9	1.00	0.00	CF,**91**,21,1992
18.	$CH_2(S) + C_2H_2 = H_2CCCH + H$	1.80E+14	0.00	0.00	BBPC,**92**,674,1988

JPC = J. Phys. Chem.; JPCRD = J. Phys. Chem. Ref. Data; SICP = Symposium International Combustion Proceedings; IJCK = Int. J. Chem. Kin. ; CPL = Chem. Phys. Lett. ; CF = Comb. Flame; BBPC = Ber. Bunsenges. Phys. Chem.; JCP = J. Chem. Phys.

(a) $[M] = \sum \varepsilon_i [c_i]$ where ε_i represents the chaperon efficiency and $[c_i]$ represents the concentration of the i^{th} species. (b) $\varepsilon_{CO} = 1.87$; $\varepsilon_{H2} = 1.87$; $\varepsilon_{CH4} = 2.81$; $\varepsilon_{CO2} = 3.0$; $\varepsilon_{H2O} = 5.0$ and all other species have efficiencies equal to unity. (c) Curved Arrhenius fit to Zellner rate expression, 7.1E+10 exp(0.00092 x T) cm^3/mol-sec, valid for 300K - 2500K. (d) $\varepsilon_{H2} = 2.0$; $\varepsilon_{CO} = 2.0$; $\varepsilon_{CO2} = 3.0$; $\varepsilon_{H2O} = 5.0$; and all other species have efficiencies equal to unity. (e) Troe fall - off reaction form: $F_{cent} = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^{*}) + \exp(-T^{**}/T)$ (f) Present Study. Multi-parameter fit to data of JCP,**64**,1150,1976 ; JPC,**92**,6313,1988 with $\Delta H_f(C_2H_3,298K)$ = 70.4kcal/mol and $\langle \Delta E_{down} = 175 cm^{-1} \rangle$. (g) Present Study . Lowered A-factor by a factor of two from Ref. [6] study and JPC,**97**,4427,1993. See Text. (h) Present Study. Branching ratio adjusted for model agreement with experimental data . See Text. This work was performed under the auspices of the US DOE by LLNL under contract No. W-7405-Eng-48.

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